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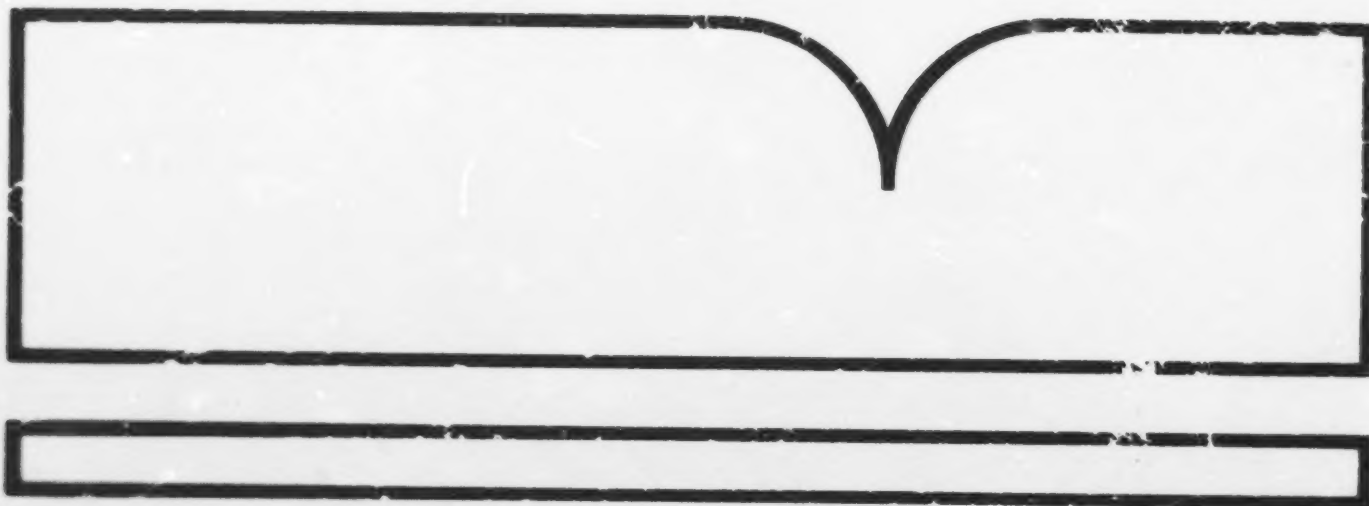
Urban Aerosol Transformation and Transport Modeling

Texas Univ. at Austin

Prepared for:

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URBAN AEROSOL TRANSFORMATION AND TRANSPORT MODELING

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## ABSTRACT

Modules for secondary aerosol formation have been included in the urban scale K-theory aerosol model, AROSOL. These are: (1) An empirical first-order SO<sub>2</sub> conversion scheme due to Meaghers, termed EMM; (2) The lumped parameter kinetic model termed the Carbon Bond Mechanism, in the version CBM-IV; (3) The lumped parameter kinetic model termed the Atkinson Lloyd Mechanism (ALM), in the 1985 ERT version; (4) The equilibrium Model for an Aerosol Reacting System (MARS) for prediction of equilibrium partition of nitrates, sulfates, and ammonium between the gas and aerosol phases; (5) The Binary Aerosol Dynamics Model (BADM) for nucleation and growth of secondary aerosol.

The modules for secondary sulfate and nitrate formation have been demonstrated with data from the 1982 Philadelphia Aerosol Field Study (PAFS). This includes a comparison of sulfate conversion as given by EMM and CBM and the available PAFS data base for a twelve hour period on 8.2.82. Both EMM and CBM give secondary sulfate concentrations whose contours are very similar and which differ mainly in the magnitudes of these concentrations. EMM was found to give secondary sulfate concentrations around ten times those with CBM. A limited comparison was carried out on the performance of the ERT ALM and CBM. For some species, the ERT ALM was found to give concentrations some 10 - 100 times those given by CBM; this finding is consistent with previous reports in the literature comparing these two models. The interpretation of these various differences is not possible owing to the lack of detailed information for the NMOC in the PAFS data base. For this same study period, MARS was used to demonstrate secondary sulfate speciation from the conversions given by CBM; as would be expected, the gas sulfate is very small and virtually all the sulfate resides in the aqueous aerosol. Also from the CBM calculations, nitrate speciation calculated by MARS was also obtained. Based on the assumed background ammonia levels, MARS predicts that all the nitrate resides in the gas phase with no aqueous or particulate nitrate; the relative humidity during this period was approximately 50%, a value too small to shift the equilibrium toward aqueous phase ammonium nitrate. It is possible that these findings would need to be modified if contributions of nitrate and sulfate from background and fumigation had been considered.

A major difficulty in this model study was the large sulfate and nitrate background during the PAFS period. For model input it was necessary to estimate background concentrations from a limited number of PAFS stations outside the modeling domain. For fumigation, no measurements were available and estimates had to be made from comparison of model predictions and observations for a "typical" day.

In all the simulations with CBM for sulfate, low sulfate formation in the modeling domain was found. There are a number of possible reasons for this. First, the hydrocarbon data from PAFS are known to be inaccurate; water interferences are now known to have been present in the analyzers; this results in hydrocarbon values that are too low. Therefore, the resultant sulfate conversion/deposition rates are too small. Also, with limited data on hydrocarbon speciation available, assumptions according to the EKMA procedure were necessary; these assumptions may not have been valid for the modeling domain. Finally, the large differences in sulfate conversion given by the CBM and ERT ALM models indicate uncertainties in applying current kinetic models.

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# LIST OF SYMBOLS

|           |                                                                                               |
|-----------|-----------------------------------------------------------------------------------------------|
| $C_i$     | gas phase concentration, $\text{kg m}^{-3}$                                                   |
| $f_i$     | lognormal frequency for species $i$ , $\text{kg}^{-1}$                                        |
| $G_i$     | particle growth rate for component $i$ , $\text{kg sec}$                                      |
| $K$       | eddy diffusivity, $\text{m}^2 \text{sec}^{-1}$                                                |
| $M_{ij}$  | binary aerosol moment function, unit depends on subscript $ij$                                |
| $m_i$     | species $i$ aerosol particle mass, $\text{kg}$                                                |
| $m_{avi}$ | mean mass species $i$ in lognormal frequency function, $\text{kg}$                            |
| $\mu_i$   | geometric standard deviation for species $i$                                                  |
| $n$       | aerosol binary number density function, $\# \text{m}^{-3} \text{kg}^{-2}$                     |
| $R_{12}$  | binary homogeneous nucleation rate density, $\# \text{m}^{-3} \text{sec}^{-1} \text{kg}^{-2}$ |
| $R_t$     | binary homogeneous nucleation rate, $\# \text{m}^{-3} \text{sec}^{-1}$                        |
| $t$       | time, $\text{sec}$                                                                            |
| $x$       | horizontal Eulerian coordinate, $\text{km}$                                                   |
| $y$       | horizontal Eulerian coordinate, $\text{km}$                                                   |
| $z$       | vertical Eulerian coordinate, $\text{km}$                                                     |

#### NOTICE

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## SECTION 1

### INTRODUCTION

The adverse effects of urban air pollution are well known: increased incidence of respiratory diseases, reduced visibility, economic loss, and inadvertent weather modification, to name a few. The urban aerosol plays an important role in these adverse effects. An understanding of this role requires, among other factors, knowledge of the aerosol dynamical processes shaping the aerosol size and composition distributions. These dynamical processes include advection, dispersion, deposition, primary and secondary source input, nucleation, condensation/evaporation, and coagulation. Models for the particle size and composition distributions reflecting these dynamical processes will ultimately be necessary for development of realistic aerosol air quality regulations and control strategies. For example, the deposition pattern of particles in the lung is a function of the particle size distribution. Absorption and scattering of light by the ambient aerosol is a complex function of the composition distribution. Many of the chemical species making up the urban aerosol are produced through the interaction of complex chemical processes and the ambient aerosol, the details of which vary with particle size and composition. Therefore, the effects of pollutant emissions reduction and control are likely to be nonlinear in character and will require the detailed knowledge cited.

This project has been concerned with development of urban aerosol models which include the dynamical processes shaping the aerosol size and composition distributions. The first part of this work has involved evaluation of data bases and a K-theory model, termed AROSOL, for the super-and sub-micrometer aerosol mass concentration. Recent work has been devoted to inclusion and development of computer modules for accurate description of the coagulation and condensation/evaporation processes for single component aerosols. Current work has proceeded along several lines. The data bases from the EPA Philadelphia Aerosol Field Study (PAFS) have been evaluated and corrected for evaluation of AROSOL for sulfate aerosol modeling. Modules have been included in AROSOL which can account for chemical conversion, nucleation, condensation, evaporation, and coagulation as a step in the extension of AROSOL to multicomponent aerosols. Work has been done on coupling the nucleation and condensation/evaporation processes to a suitable oxidant mechanism for sulfate and nitrate formation.

This report begins with a description of AROSOL and discussion of the chemical and aerosol modules that are available. In particular, the binary aerosol dynamics model (BADM), suitable for binary nucleation and growth studies, is presented in detail because only an outline of the model has been given in the literature. The modules for secondary sulfate and nitrate formation have been demonstrated with data from the 1982 Philadelphia Aerosol Field Study (PAFS). This report closes with a discussion of future research problems in urban aerosol modeling. In particular, the need for subgrid scale models and refinement of existing kinetic models to handle reactive plumes is pointed out.

## SECTION 2

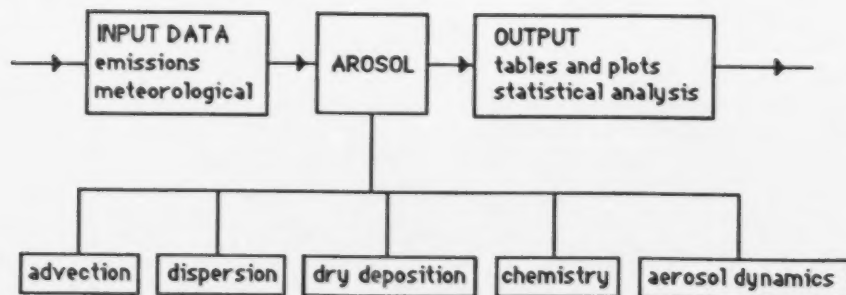
### DESCRIPTION OF AROSOL

AROSOL is an urban scale K-theory model for the ambient atmospheric aerosol. It has been previously used in a number of studies including modeling total aerosol mass concentration in Maricopa County, Arizona<sup>1</sup>, super- and sub-micrometer aerosol mass concentration in St. Louis, Missouri using the Regional Air Pollution Study (RAPS) data base<sup>2</sup>, and more recently a study of sulfate transport and transformation using the EPA Philadelphia Aerosol Field Study data base<sup>3</sup>. The extension of the model to include secondary sulfate and nitrate aerosol sources is described here. First the various components of AROSOL will be presented. This is followed by detailed discussion of the various modules available in AROSOL. Here, the recent work is summarized on inclusion of oxidant chemistry for the gas phase conversion of sulfur dioxide to sulfates and nitrogen oxides to nitrates, inclusion of MARS<sup>4</sup> for equilibrium partitioning of sulfates and nitrates between the gas phase and particulate phase, and inclusion of a general model for binary particle formation by homogeneous nucleation and growth.

#### GENERAL DESCRIPTION

AROSOL is arranged with a number of options for inclusion of meteorological data ranging from a single measurement of wind speed and direction to time series of data on wind speed and direction and atmospheric stability.

The structure of AROSOL can be indicated by the schematic diagram shown below.



As indicated, data input includes emissions inventory data and meteorological data. Emissions inventory data are entered from tape or other data storage media. Meteorological data may be entered externally from data storage media or, in the case of limited meteorological data, may be entered internally through data statements. The model has provision for inferring complete wind field and stability conditions over a study area for a range of data availability from measurements at a single point to complete time series at multiple points.

Results from AROSOL simulations may be displayed in various forms including tabular data, isopleth plots, and full three dimensional plots. Modules are available for analysis of simulation results and measurement data including statistical analysis options for model evaluation as recommended by EPA as well as spectral analysis. New analytical modules will be included as available.

The various rate modules of AROSOL are indicated in the diagram above. The Eulerian grid consists of horizontal  $x,y$  UTM coordinates and a vertical sigma,  $s$ , coordinate<sup>4</sup> for simulation of complex terrain. The horizontal grid is usually employed with a variable mesh with highest density in the regions of large sources. Usually, no more than the order of 14 vertical levels of variable thickness are employed. Time splitting<sup>5</sup> is employed based on the process.

The  $x,y$  boundary conditions are specified depending on whether the wind is flowing into or out of the modeling region. For wind flowing out of the modeling region a constant flux conditions in  $x,y$  is imposed. For wind flowing into the modeling region, the appropriate pollutant variable must be imposed; these values must be set from background assumptions or actual upstream measurements. The boundary condition at the surface is discussed below under the section on dry deposition. The upper level boundary condition is usually specified by a zero flux condition at the mixing height which is specified from field data. It is possible to allow for entrainment through the upper boundary but this must be done empirically.

The rate modules indicated in the diagram above will now be discussed in order.

## RATE MODULES

### Advection

The advection term in the conservation equation is evaluated numerically using the iterated upstream finite difference scheme proposed by Smolarkiewicz<sup>6</sup>. This scheme is used because it maintains the conservation and positiveness of transported conservative species reasonably well. The scheme is also relatively fast compared to other methods with similar conservation properties. In addition the scheme is local in that the advective time change at a point is determined by the concentrations and velocities at a small number of neighboring points.

### Dispersion

The vertical and horizontal diffusivity terms are handled by orthogonal collocation on finite elements. This scheme has been found to provide reasonable accuracy and efficiency in dispersion simulations<sup>7</sup>.

It is widely recognized that the eddy diffusivities are not fluid properties but are functions of the dynamical state of the atmosphere. Therefore the eddy diffusivities are empirical constructs which must be specified for various atmospheric states. For all but small advective flows, horizontal diffusivity,  $K_H$ , is relatively unimportant compared to advection as a transport mechanism; this is fortunate since an adequate parameterization of this coefficient is lacking. In AROSOL,  $K_H$  is chosen as  $50 \text{ m}^2/\text{sec}$ . The vertical diffusivity,  $K_V$ , is often the dominant mechanism for vertical transport.  $K_V$  is calculated from the friction velocity and Monin-Obukhov length. These parameters are specified by the stability class, the ground level wind speed, the surface roughness, the height of the wind measurements, and the height of the grid cell. Atmospheric stability is based on the Pasquill atmospheric stability class. Parameterizations of  $K_V$  for stable<sup>8</sup>, neutral and unstable<sup>9</sup> conditions are employed.

In order to prevent artificial diffusion, for point sources and area sources below the size of the x,y grid, a subgrid scale Gaussian plume model is used. The source is dispersed by this model until 90% of the plume fills one of the grid dimensions. At this point, the plume is assigned to the grid nodes.

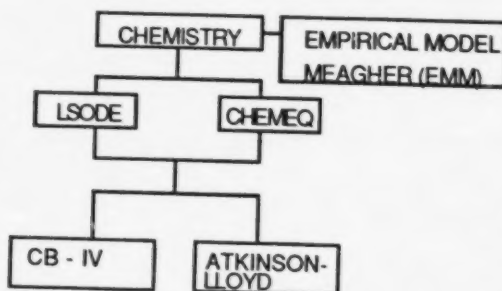
### Dry Deposition

At the surface, the boundary condition is specified by parameterizations of deposition velocities. For gases, surface resistances are scaled from field data for  $\text{SO}_2$ . For submicrometer and particulate sulfate, a parameterization from Wesely and Shannon is used<sup>10</sup> for the deposition velocity. Deposition velocities

for supermicrometer particles are estimated using procedures we have previously evaluated <sup>1,2</sup>.

### Chemistry

AROSOL offers several options in the calculation of the homogeneous gas phase conversion of SO<sub>2</sub> to sulfate. This is indicated in the diagram below.



One of these is an empirical first-order decay model from Meagher<sup>11</sup> (EMM) . Two mechanistic semi-empirical modules are also included which attempt to model atmospheric photochemistry. These are the carbon bond mechanism (CBM) <sup>12</sup> suitably modified for sulfate conversion and the Atkinson and Lloyd mechanism (ALM) <sup>13</sup>. Two options are indicated for integrating the kinetic rate equations for these two models: the stiff system integrator known as LSODE and a faster, but less accurate integrator known as CHEMEQ; these will be discussed below. Several aerosol modules have been included in AROSOL. One of them, MARS (Model for an Aerosol Reacting System) <sup>4</sup>, may be used to estimate the aqueous phase oxidation of sulfur dioxide in the presence of hydrogen peroxide, ozone and catalytic cations.

### Empirical Model of Meagher--

The empirical model of Meagher<sup>11</sup> (EMM) is based on field measurements. Its simplicity and computational efficiency make it appealing for first-order estimates of sulfate formation rates when the amount of reliable input data is limited. Details of EMM will not be given here. These details are available in earlier reports<sup>3</sup> describing use of EMM in urban simulations.

EMM is based loosely on the diurnal and annual variation in clear-sky solar intensity. The basic assumption is that the rate constant for sulfate conversion

can be separated into a constant value and a component that is allowed to vary diurnally and annually. The various parameters in EMM were derived from a consistent set of data from multiple field studies conducted in each of four seasons to optimize the parameters. The model was formulated to give an average over these field results and it cannot be supposed that it will exhibit skill in reproducing individual events. It will be predictive only insofar as events to be modeled with it are within the same reactive regimes. The field studies used for derivation of EMM represent on the whole rural conditions. Therefore, EMM must be applied with caution in urban simulations; results from its use are to be regarded as guides in carrying out simulations with the more complex and computationally demanding models, CBM and ALM.

#### CBM-IV mechanism--

Some detail will be given here on the CBM mechanism, as this is the model preferred by EPA in urban simulations and CBM has been modified in AROSOL according to recommendations from EPA. In the CBM, organic species are grouped according to type and number of carbon bonds in the molecule irrespective of the particular chemical species in which the bond is found. The structural classes have been determined through the use of structural reactivity analysis. The lumping of organic species in the CBM becomes transparent if one examines the scheme for CBM-IV shown in Table 1 below.

The carbon bond mechanism has several advantages over other lumped mechanisms. To name a few, it conserves carbon atoms, it has a narrow range of reactivities for a group of lumped species, and the reactivity of the organic mixture changes in a natural way. The mechanism follows the reactions of the lumped species. The rate constants for these species are obtained by averaging the rate constants for the individual species that comprise the lumped identity. The reactivity of an organic mixture changes according to the concentrations of the different bond types in the carbon mechanism.

CBM uses a hierarchy of chemical species in which each species involved in oxidant formation is assigned a hierarchical level on the basis of the number of systems in which it occurs. This is illustrated schematically in the figure below.

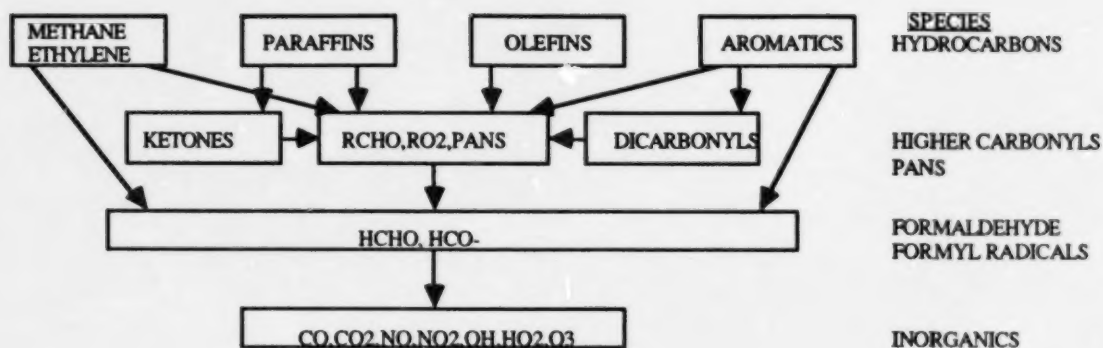


Fig. 1 Schematic diagram of hierarchical levels of chemical species in photochemical smog.

AROSOL includes CBM-IV which is a condensed version of the larger CBM-X mechanism<sup>14</sup>. This condensed version is suitable for use in a computationally demanding model such as AROSOL in an urban or regional area.

Table 1 contains the version of CBM-IV that is currently used in EPA's Regional Oxidant Model (ROM2.0) plus a sulfate formation mechanism that excludes the reactions of the Criegee intermediates. The Criegee intermediates, which can react with  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$  would only be important when the hydrocarbon to nitrogen oxides ratio is very large and at the same time the relative humidity is very low; these conditions are not thought to be common in urban areas. The photolytic reactions are #s 1, 8, 9, 19, 24, 28, 33, 34, 40, and 47. The rates of most of these reactions are known to vary with zenith angle in a fashion similar to the photolysis of  $\text{NO}_2$ . Therefore, the rate constants for these reactions are expressed as a multiple of the photolytic constant for  $\text{NO}_2$ . The photolysis of  $\text{O}_3$  to  $\text{O}(^1\text{D})$  (reaction #8) and the photolysis of formaldehyde and acetaldehyde (reactions 33, 34, and 40) vary with zenith angle in a manner dissimilar to that of  $\text{NO}_2$ , and they are therefore treated differently in the mechanism. Reactions 71 to 75 are added to account for photochemical conversion of  $\text{SO}_2$  after the scheme proposed by Meagher<sup>11</sup>. Table 2 interprets the symbols used in Table 1.

Up to now we have not mentioned an important problem in modeling atmospheric chemical reactions such as shown in Table 1. This is the fact that these reactions occur in a turbulent environment. This problem is well known<sup>9,15,16</sup> and poses obvious difficulties in applying first order closure to

second order reactions when the characteristic reaction times are much less than the Lagrangian time scale of the turbulence. For regional scale models when concentration levels of reactants are low, these considerations may be less important than for urban scale models near sources. Accounting for correlation effects on the chemical reaction rates would require sub-grid scale modeling.

TABLE 1. THE CARBON BOND MECHANISM -- IV

| Reactions |                                     |                                     | Rate Constant | Activation Energy |
|-----------|-------------------------------------|-------------------------------------|---------------|-------------------|
| 1         | NO <sub>2</sub>                     | = NO + O                            | VARY          |                   |
| 2         | O                                   | = O <sub>3</sub>                    | 4.35E6        | -690.             |
| 3         | O <sub>3</sub> + NO                 | = NO <sub>2</sub>                   | 26.6          | 1430.             |
| 4         | O + NO <sub>2</sub>                 | = NO                                | 13800.        |                   |
| 5         | O + NO <sub>2</sub>                 | = NO <sub>3</sub>                   | 2320.         | -600.             |
| 6         | O + NO                              | = NO <sub>2</sub>                   | 3120.         | -411.             |
| 8         | O <sub>3</sub>                      | = 0.205 OH + 0.897 O                | VARY          |                   |
| 9         | O <sub>3</sub>                      | = O                                 | 0.0421xk1     |                   |
| 10        | O <sub>3</sub> + OH                 | =HO <sub>2</sub>                    | 100.          | 940.              |
| 11        | O <sub>3</sub> + HO <sub>2</sub>    | = OH                                | 3.            | 580.              |
| 12        | NO <sub>3</sub> + NO                | = 2 NO <sub>2</sub>                 | 28100.        | -250.             |
| 13        | NO <sub>3</sub> + NO <sub>2</sub>   | = NO + NO <sub>2</sub>              | 0.59          | 1230.             |
| 14        | NO <sub>3</sub> + NO <sub>2</sub>   | = N <sub>2</sub> O <sub>5</sub>     | 1780.         | 60.               |
| 15        | N <sub>2</sub> O <sub>5</sub>       | = 2 HNO <sub>3</sub>                | 0.0285        |                   |
| 16        | N <sub>2</sub> O <sub>5</sub>       | = NO <sub>3</sub> + NO <sub>2</sub> | 3.12          | 10840.            |
| 17        | NO + NO <sub>2</sub>                | = 2 HNO <sub>2</sub>                | 2.4E-7        |                   |
| 18        | HNO <sub>2</sub> + HNO <sub>2</sub> | = NO + NO <sub>2</sub>              | 1.5E-5        |                   |
| 19        | HNO <sub>2</sub>                    | = NO+ OH                            | 0.18xk1       |                   |
| 20        | NO <sub>2</sub> + OH                | = HNO <sub>3</sub>                  | 16300.        | -560.             |
| 21        | NO + OH                             | = HNO <sub>2</sub>                  | 9770.         | -427.             |
| 22        | HO <sub>2</sub> + NO                | = OH + NO <sub>2</sub>              | 12300.        | -240.             |
| 23        | NO + NO                             | = 2 NO <sub>2</sub>                 | 1.52E-4       | -530.             |
| 24        | H <sub>2</sub> O <sub>2</sub>       | = 2 OH                              | .0014xk1      |                   |
| 25        | OH + H <sub>2</sub> O <sub>2</sub>  | = HO <sub>2</sub>                   | 2520.         | 187.              |
| 26        | OH + HNO <sub>2</sub>               | = NO <sub>2</sub>                   | 9770.         |                   |
| 27        | OH + HNO <sub>3</sub>               | = NO <sub>3</sub>                   | 192.          | -778              |

|    |             |                                                                               |         |        |
|----|-------------|-------------------------------------------------------------------------------|---------|--------|
| 28 | NO3         | = 0.85NO2 + 0.85O + 0.15NO                                                    | 30.6xk1 |        |
| 29 | HO2 + HO2   | = H2O2                                                                        | 4144.   | -1150  |
| 30 | HO2 + HO2   | = H2O2                                                                        | 3270.   | -5800. |
| 31 | OH + CO     | = HO2                                                                         | 400.    |        |
| 32 | FORM + OH   | = HO2 + CO                                                                    | 15000.  |        |
| 33 | FORM        | = 2HO2 + CO                                                                   | VARY    |        |
| 34 | FORM        | = CO                                                                          | VARY    |        |
| 35 | FORM + O    | = OH + HO2 + CO                                                               | 237.    | 1550.  |
| 36 | FORM + NO3  | = HNO3 + HO2 + CO                                                             | 0.93    |        |
| 37 | ALD2 + O    | = C2O3 + OH                                                                   | 636.    | 986.   |
| 38 | ALD2 + OH   | = C2O3                                                                        | 24000.  | -250.  |
| 39 | ALD2 + NO3  | = C2O3 + HNO3                                                                 | 3.7     |        |
| 40 | ALD2        | = XO2 + 2HO2 + CO + FORM                                                      | VARY    |        |
| 41 | ALD2 + HO2  | = XO2 + 2 FORM + HO2                                                          | 5.      |        |
| 42 | C2O3 + NO   | = NO2 + XO2 + FORM + HO2                                                      | 16500.  | -250.  |
| 43 | C2O3 + NO2  | = PAN                                                                         | 9000.   | -250.  |
| 44 | PAN         | = C2O3 + NO2                                                                  | 0.0222  | 14000. |
| 45 | C2O3 + C2O3 | = 2XO2 + 2FORM + 2HO2                                                         | 3700.   |        |
| 46 | C2O3 + HO2  | =                                                                             | 9600.   |        |
| 47 | MGLY        | = C2O3 + HO2 + CO                                                             | 0.02xk1 |        |
| 48 | MGLY + OH   | = XO2 + C2O3                                                                  | 26000.  |        |
| 49 | CH          | = XO2 + FORM + HO2                                                            | 21.     |        |
| 50 | PAR + OH    | = 1.49XO2 + 0.067XO2N + 0.93HO2 +<br>+ 0.45ALD2 - 0.75PAR                     | 1150.   |        |
| 51 | O + OLE     | = 0.95ALD2 + 0.35HO2 + 0.2XO2 +<br>0.15CO + 0.05FORM + 0.05C2O3 +<br>-0.35PAR | 5920.   | 324.   |
| 52 | OH + OLE    | = FORM + ALD2 + XO2 + HO2 - PAR                                               | 42000.  | -537.  |
| 53 | O3 + OLE    | = 0.5ALD2 + 0.66FORM + 0.212CO +<br>0.28HO2 + 0.144XO2 + 0.08OH - PAR         | 0.018   | 1897.  |
| 54 | NO3 + OLE   | = 0.91XO2 + 0.91HO2 + 0.09XO2N                                                | 11.4    |        |
| 55 | O + ETH     | = FORM + XO2 + CO + 2HO2                                                      | 1080.   | 800.   |
| 56 | OH + ETH    | = XO2 + 2FORM + HO2                                                           | 12000.  | -382.  |
| 57 | O3 + ETH    | = FORM + 0.37CO + 0.13HO2                                                     | 0.0027  | 2840.  |

|    |                    |                                                                                     |         |        |
|----|--------------------|-------------------------------------------------------------------------------------|---------|--------|
| 58 | TOL + OH           | = HO2 + 0.64XO2 + 1.13FORM +<br>0.56MGly + 0.36PHEN+ 0.36PAR<br>+ 1.13CO            | 9750.   |        |
| 59 | PHEN + NO3         | = PHO + HNO3                                                                        | 14000.  |        |
| 60 | PHO + NO2          | =                                                                                   | 20000.  |        |
| 61 | XYL + OH           | = HO2 + 0.72XO2 + 0.67CO + 1.33MGly<br>+ 0.28PHEN + 0.56PAR + 0.06TLA<br>+ 0.67FORM | 36000.  |        |
| 62 | TLA + OH           | = XO2 + PHO + 2PAR                                                                  | 20000.  |        |
| 63 | ISOP + O           | = HO2 + 0.8ALD2 + 0.55OLE +<br>0.5XO2 + 0.5CO + 0.45ETH<br>-0.1PAR                  | 28000.  |        |
| 64 | ISOP + OH          | = 0.87XO2 + 0.87FORM + 0.87HO2<br>+ 0.29PAR + 0.29OLE + 0.58ETH<br>+ 0.29ALD2       | 126000. |        |
| 65 | ISOP + O3          | = FORM + 0.45ALD2 + 0.55ETH<br>+ 0.98HO2 + 0.1OLE + 0.06CO<br>-0.25PAR              | 0.018   |        |
| 66 | ISOP + NO3         | = XO2N                                                                              | 165.    |        |
| 67 | XO2N + NO          | =                                                                                   | 1000.   |        |
| 68 | XO2 + NO           | = NO2                                                                               | 12000.  |        |
| 69 | XO2 + HO2          | =                                                                                   | 5000.   | -1300. |
| 70 | XO2 + C2O3         | = XO2 + NO2 + FORM                                                                  | 2400.   |        |
| 71 | HO + SO2 +(O2,H2O) | = HO2 + H2SO4                                                                       | 1496.   |        |
| 72 | HO + SO2 +(O2)=    | HSO5                                                                                | 23.     |        |
| 73 | HSO5 + NO          | = NO2 + HSO4                                                                        | 10268.  |        |
| 74 | HSO4 + HO2         | = H2SO4 + O2                                                                        | 256.    |        |
| 75 | HSO4 + O3          | = HSO5 + O2                                                                         | 10.     |        |

---

Rate constants in ppm min units at 298K. Activation energies are B in  
expression

$$k_T = k_{298} \exp(B(1/298 - 1/T)).$$

TABLE 2 . SPECIES USED IN MODIFIED CBM-IV MECHANISM

| Mechanistic symbol | Name                          |
|--------------------|-------------------------------|
| NO                 | NITRIC OXIDE                  |
| NO2                | NITROGEN DIOXIDE              |
| NO3                | NITROGEN TRIOXIDE             |
| N2O5               | DINITROGEN PENTOXIDE          |
| HNO2               | NITROUS ACID                  |
| HNO3               | NITRIC ACID                   |
| O                  | ATOMIC OXYGEN (O3P)           |
| O3                 | OZONE                         |
| OH                 | HYDROXYL RADICAL              |
| HO2                | HYDRO PEROXY RADICAL          |
| CO                 | CARBON MONOXIDE               |
| H2O2               | HYDROGEN PEROXIDE             |
| PAN                | PEROXYACYL NITRATE            |
| FORM               | FORMALDEHYDE                  |
| ALD2               | ACETALDEHYDE                  |
| MGLY               | METHYL GLYOXAL                |
| PAR                | PARAFFIN CARBON BOND          |
| OLE                | OLEFIN CARBON BOND            |
| ETH                | ETHYLENE                      |
| TOL                | TOLUENE SURROGATE             |
| XYL                | XYLENE SURROGATE              |
| TLA                | TOLUALDEHYDE SURROGATE        |
| ISOP               | ISOPRENE                      |
| C2O3               | PEROXY ACYL RADICAL           |
| PHEN               | PHENOL (CRESOL) SURROGATE     |
| PHO                | PHENOXY RADICAL SURROGATE     |
| XO2                | PEROXY RADICAL                |
| XO2N               | PEROXY NITRATE                |
| HSO4               | HYDROGEN SULFATE FREE RADICAL |
| HSO5               | HYDROXYSULFATE FREE RADICAL   |
| H2SO4              | SULFURIC ACID                 |

In urban modeling using AROSOL, the solution of the set of differential equations in CBM or ALM accounts for a significant part of the CPU time in the computation. The reaction rate equations must be integrated for each grid point in the simulation for relatively short time periods between the steps for the transport processes. Therefore, self-starting methods with low start-stop overhead are required. Also, the large number of nodes in the simulation usually precludes storing auxiliary information for the spatial grid points between time steps. Since much of the computer time would be spent starting a higher order method, low-order methods are almost always more flexible and run faster. Another consideration is the fact that CBM and ALM are both semi-empirical models which undoubtedly will be modified in the future; therefore, we prefer to use a general integration method instead of a specialized program devised to integrate efficiently only CBM or ALM. With all these points in view, we have adopted a numerical technique known as CHEMEQ<sup>17</sup>. This is a second-order predictor, iterated-corrector scheme which involves an "asymptotic" treatment for equations which the technique determines are stiff. The method is self-starting and an appropriate time step is automatically chosen to give results of specified accuracy. The advantage of using CHEMEQ is evident from Fig. 2 showing computation time in AROSOL using CHEMEQ and a standard stiff integrator known as LSODE. Fig. 3 shows that very little sacrifice is made in accuracy using CHEMEQ and that the decrease in accuracy is less than other errors expected in urban modeling. These calculations were made for the following initial concentrations, all in ppm: NO<sub>2</sub>=0.022, NO=0.009, SO<sub>2</sub>=0.053, O<sub>3</sub>=1.33, CO=1.15, CH<sub>4</sub>=0.1, ETH=0.1, PAR=0.1. The effect of including emissions has not been examined and may alter these reported CPU times. Also, it must be pointed out that pathological initial conditions exist leading to very stiff equations; in these cases CHEMEQ may not be sufficiently accurate even for urban modeling applications. On balance, CHEMEQ represents the best integrator we have found for chemical kinetics modeling in AROSOL but it should always be tested initially with the accurate integrator, LSODE. AROSOL has the capability of providing this test.

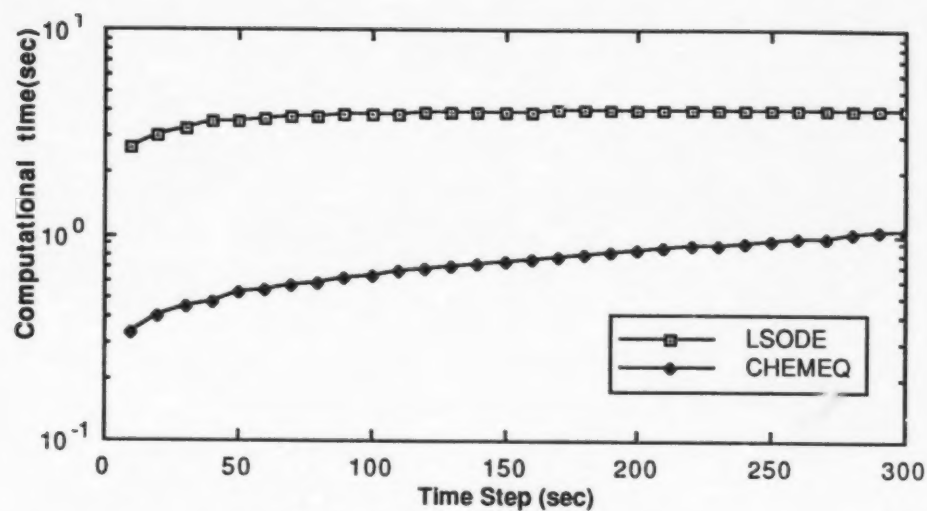


Fig. 2 Comparison of computation times

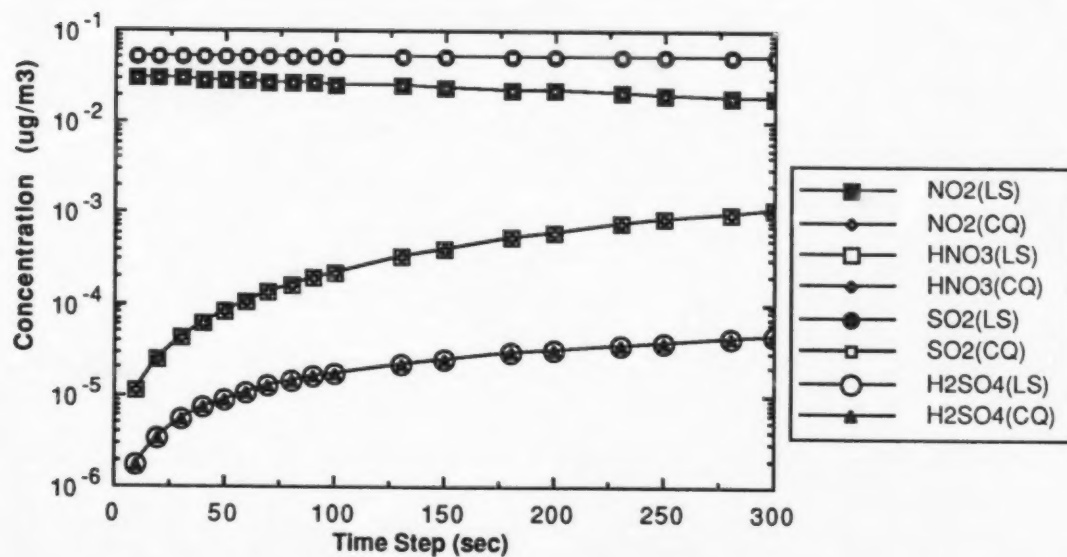
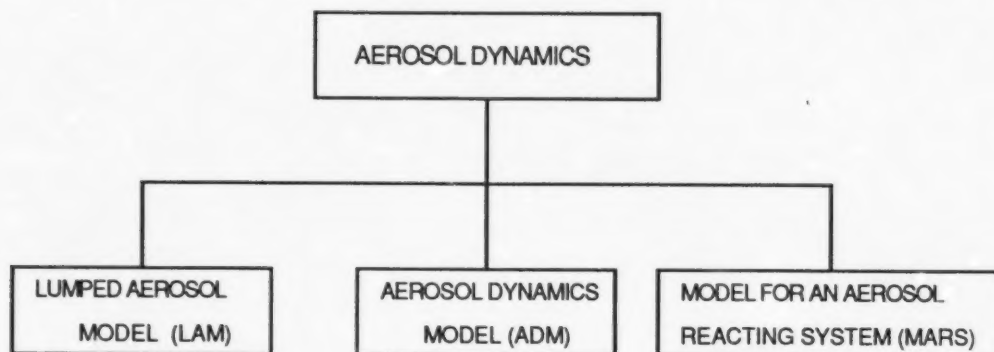


Fig. 3 Comparison of integration methods (LS)=LSODE, (CQ)=CHEMEQ

### Aerosol Dynamics

The term aerosol dynamics in the present context refers to the processes of nucleation, heterogeneous reactions, condensation, evaporation, and coagulation. These processes alter the size and composition distributions of the ambient atmospheric aerosol. The eventual need for knowledge of these distributions in the regulatory process has been discussed briefly in Section 1. Apart from this, knowledge of the aerosol dynamics is essential to a basic understanding of the complex atmospheric and chemical processes and their effects involved in atmospheric pollution.

A schematic diagram of the options available in AROSOL is given below.



These various options will now be discussed.

Some of the reaction products resulting from the homogeneous gas phase photochemical reactions will remain in the gas phase owing to their relatively high vapor pressure. Sulfuric acid, due to its relatively low vapor pressure (normal boiling point  $> 300^{\circ}\text{C}$ ) and reactivity, will partition predominantly to the aerosol phase in the atmosphere. Under the relatively high concentrations of sulfur dioxide, nitrogen oxides and hydrocarbons found in urban areas near to sources, binary nucleation involving sulfuric acid and water can occur. At the lower concentration levels found for example in regional modelling applications, sulfuric acid most likely will react with or condense onto the existing atmospheric aerosol or will be formed by heterogeneous conversion in aqueous aerosol and cloud droplets. Nitric acid has a relatively high vapor pressure (normal boiling point  $86^{\circ}\text{C}$ ) and is therefore unlikely to undergo a phase transition (nucleate) at typical temperatures and conversion rates found in the atmospheric boundary

layer. Sulfuric and nitric acids will of course react with gases such as ammonia. In this case, nitrate will partition between the gas and aerosol phases.

#### Model for an Aerosol Reacting System (MARS) -

The Model for an Aerosol Reacting System (MARS) <sup>4</sup> was developed to provide an *equilibrium* model for prediction of mass and chemical composition of atmospheric aerosols containing sulfate, nitrate, ammonium and water. MARS can also be used to treat aqueous phase oxidation of sulfur dioxide to sulfate by hydrogen peroxide, ozone and Mn and Fe cation catalysts. MARS provides a convenient and rapid estimate of partitioning of the stated species between aerosol and gas phase. However, it must be noted that the model does not address possible alteration of this partitioning by other existing aerosol constituents and it also does not account for creation of new particles by homogeneous nucleation. The latter process cannot be ruled out at urban pollutant levels.

#### Dynamic aerosol models -

There are two limits in the approach to modeling the dynamics of secondary aerosol formation in the atmosphere and the interaction of this aerosol with the primary aerosol. In one approach, termed here the lumped aerosol model (LAM), a species such as sulfate is emitted from primary sources, created by atmospheric reactions, advects and disperses, and undergoes deposition processes in an analogous manner to gaseous species. In the LAM, empirical parameterizations of some of the size dependent aerosol processes, such as dry deposition, are necessary. In LAM there is also no possibility of describing the interaction between secondary and primary aerosol unless empirical correlations are used. The other approach deals with particle size and composition distributions and attempts to account for all the aerosol dynamics processes--an approach termed here the aerosol dynamics model (ADM). This approach, at least in principle, does not require any empirical aerosol rate information.

AROSOL has the option of using either the LAM or ADM. The LAM and ADM options as they exist with AROSOL will now be discussed.

#### Lumped aerosol model (LAM) --

LAM treats species, such as sulfate, that deposits entirely in the aerosol phase, as simply additional chemical species. The rationale for this approach has been shown explicitly<sup>2</sup>. The contributions to the rate processes for these species may be indicated schematically:

rate of change of species

$$\begin{aligned} \text{mass concentration} = & (1) \text{ (rate of change due to advection)} \\ & + (2) \text{ (rate of change due to dispersion)} \\ & + (3) \text{ (rate of change due to sedimentation)} \\ & + (4) \text{ (rate of change due to deposition)} \\ & + (5) \text{ (rate of change due to condensation)} \\ & + (6) \text{ (rate of change due to homogeneous nucleation)} \end{aligned}$$

It may be noted that the coagulation process does not enter since the mass concentration is conserved by coagulation; coagulation does not alter the mass concentrations, but merely changes the composition distribution. It is always observed in atmospheric aerosol simulations that particles less than the order of 2 micrometers evolve independently of the larger particles and that particle growth processes arising from homogeneous nucleation, condensation and coagulation do not affect the larger particles<sup>2</sup>. Therefore, the mass concentration may be regarded as being made up of two independent fractions: particles greater than approximately 2 micrometers produced by primary sources and those smaller, the so-called "fine particles" that arise both from primary source input and secondary sources. Sedimentation is unimportant for the fine particle fraction. It is in consideration of rate processes 4,5 and 6 that the deficiency of the LAM approach is clear. Deposition and condensation rates are dependent on particle size. A deposition rate must be obtained empirically to close the mass conservation equation; however, this deposition rate will be dependent on the size distributions existing during the field measurements and may not be applicable at other locations or times. In the LAM approach, the distinction between condensation and homogeneous nucleation is ignored. If heterogeneous conversion processes are negligible, the rate of formation of a species' particulate mass concentration is assumed to be equal to the rate of production of vapor phase mass concentration by chemical reaction. For those species depositing entirely in the aerosol phase, this assumption appears to be acceptable. Of course, for a species such as nitrate, the LAM must be supplemented with an equilibrium model such as MARS.

### Binary aerosol dynamics model (BADM) --

We have developed accurate and efficient numerical schemes for simulation of coagulation and condensation/evaporation processes<sup>18,19,20,21,22</sup> and have carried out the first comprehensive studies<sup>23,24,25</sup> of aerosol growth in the context of a model for atmospheric dispersion and transport. The modules for coagulation and condensation/evaporation that have been developed have proven to yield accurate simulations of aerosol growth processes in the atmospheric models. These modules have provided the reference calculations for evaluation of more approximate calculation schemes<sup>26</sup>. This work has been done for aerosol dynamics models for the particle size or mass distribution,  $n(m,r,t)$ , where  $n(m,r,t)dm$  is the number of particles having masses in the range  $m$  to  $m+dm$  at a vector position in space,  $r$ , at time  $t$ .

We have developed accurate modules for multicomponent aerosol dynamics but these are not feasible for large scale simulations. We have also developed approximate but computationally efficient methods, which can be checked with calculations using the accurate modules.

We have shown that accurate numerical methods are available for simulation of aerosol dynamics, including the evaporation process. However, these accurate methods may not be feasible for many spatially inhomogeneous, unsteady state problems, for which computer time can be prohibitive. In addition, even for computationally feasible problems, it is desirable to have available numerical techniques that are easily and rapidly applied. Of these approximate techniques, the moment method appears most promising. Earlier work on the use of the moment method for solution of the coalescence equation has been reviewed by Drake<sup>27</sup>. Clark<sup>28</sup> reported results on numerical calculations of the cloud physical equations for condensation and coalescence using both lognormal and gamma distributions to effect closure of the moment equations. More recently, the moment method with closure by the lognormal distribution has been widely applied in analysis of aerosol dynamics<sup>29,30,31</sup>. We have recently extended for the first time the moment method to the aerosol evaporation problem<sup>32</sup>; this extension appears capable of providing reasonably accurate simulations of atmospheric aerosol evaporation.

Moment model for binary nucleation and growth --

As pointed out above, the rate of formation of sulfuric acid by photochemical reactions in urban areas can be sufficiently high that binary nucleation of sulfuric acid and water can occur. We have developed a moment method for this process<sup>33</sup> which will be described briefly here.

Binary aerosol is described by its distribution,  $n(m_1, m_2, x, y, z, t)$ , where  $ndm_1dm_2$  is the number of particles having masses of species 1 and 2 in the ranges  $m_1dm_1$  and  $m_2dm_2$  at spatial point  $x, y, z$  at time  $t$ . The evolution of  $n$  is followed through several of its moments,  $M_{ij}$ :

$$M_{ij} = \iint m_1^i m_2^j n(m_1, m_2) dm_1 dm_2 \quad (1)$$

where the integration is over all masses  $m_1$  and  $m_2$ . The moments necessary for homogeneous nucleation and particle growth are  $M_{00}$  (the total particle number concentration),  $M_{10}$ ,  $M_{01}$ ,  $M_{20}$ , and  $M_{02}$ .

For simplicity, the coagulation term will be omitted in this description; it is, however, included in the general moment formulation. When particle growth occurs by binary nucleation and condensation/evaporation processes, the evolution equation for  $n$  has the form:

$$\partial n / \partial t = - (\partial / \partial m_1)(G_1 n) - (\partial / \partial m_2)(G_2 n) + R_{12} \quad (2)$$

where  $G_1, G_2$  are the particle growth rates for 1 and 2 and  $R_{12}$  is the binary nucleation rate.

The following moment equations are derived from eqs.(1) and (2):

$$dM_{00}/dt = R_t \quad (3)$$

where

$$R_t = \iint R_{12} dm_1 dm_2$$

Also:

$$dM_{10}/dt = \iint G_1 n dm_1 dm_2 \quad (4)$$

$$dM_{01}/dt = \iint G_2 n dm_1 dm_2 \quad (5)$$

$$dM_{20}/dt = \iint m_1 G_1 n \, dm_1 dm_2 \quad (6)$$

$$dM_{02}/dt = \iint m_2 G_2 n \, dm_1 dm_2 \quad (7)$$

$$d(M_{10} + C_1)/dt = 0 \quad (8)$$

$$d(M_{01} + C_2)/dt = 0 \quad (9)$$

$C_1$  and  $C_2$  are the vapor mass concentration of species 1 and 2 respectively and eqs. (8) and (9) express mass conservation.

$G_1$  and  $G_2$  are the noncontinuum growth rates and include the Kelvin effect and activity coefficients for the mixture<sup>34</sup>. The expression for  $R_{12}$  may be taken from the classical theory of binary homogeneous nucleation with its modifications<sup>35</sup>. These modifications include nucleation in the presence of existing particles.

Eqs. (3) - (9) are not a closed set for the moments and closure is in general not possible. Closure is achieved here by using a parameterized form for the distribution  $n$ . It is assumed that in the atmosphere, the mixture of secondary and primary particles constitute an intrinsic mixture in that all particles will contain both species 1 and 2. For this case, closure is obtained with the model:

$$n(m_1, m_2) = M_{00} f_1(m_1) f_2(m_2) \quad (10)$$

where the  $f_i$  are lognormal frequencies:

$$f_i = (2\pi)^{-1/2} (1/m_i \ln \mu_i) \exp(-\ln^2(m_i/m_{avi})/2\ln^2 \mu_i)$$

and  $m_{avi}$  and  $\mu_i$  are respectively the mean mass and geometric standard deviation for species  $i$ . These parameters can be expressed in terms of the moments defined above:

$$m_{av1} = M_{10}^2 / (M_{20}^{1/2} M_{00})^{3/2}$$

$$\mu_1 = M_{00} M_{10} / M_{20}^2$$

with similar expressions for species 2.

The validity of this moment procedure has been studied in the absence of nucleation. For various growth laws,  $G_1$  and  $G_2$ , permitting analytical solutions, agreement to within less than 1% has been obtained between the moment solution and the analytical solution for the moments. For example, for the growth law,  $G_i = a_i (m_1 + m_2)^{2/3}$  the agreement for the first two moments is shown in Fig. 4, where for the constants in  $G_i$ :  $a_1 = (1/2) a_2$ .

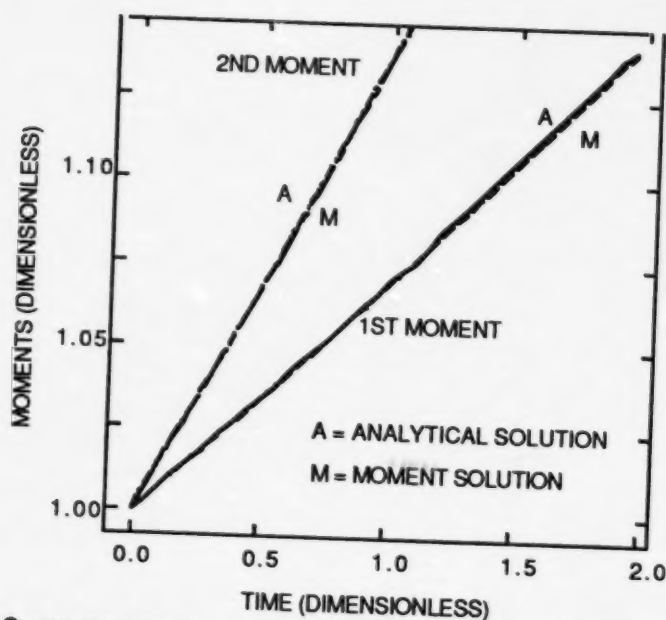


Fig. 4 Comparison of moment and analytical solutions of aerosol growth equation for the growth law,  $G_i = a_i (m_1 + m_2)^{2/3}$

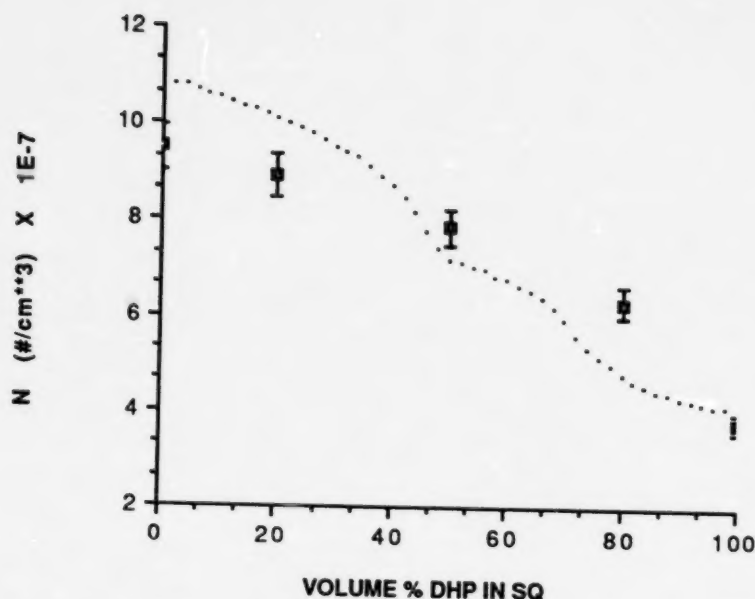


Fig. 5 Comparison of moment theory with experimental data for binary aerosol formed by homogeneous nucleation in a laminar jet. Total particle number concentration versus parent vapor mass percent dihexyl phthalate(DHP) in squalane (SQ). Points with error bars are experimental data. Dotted curve is moment theory.

This theory has been used in a comparison with experimental data for nucleation and growth of binary aerosols occurring in a laminar jet<sup>33</sup>. A comparison between moment theory and experiment for the total aerosol number concentration as a function of parent vapor concentration is shown in Fig. 5. Here, a set of data from binary aerosol formed by homogeneous nucleation of dihexyl phthalate and squalane has been used. Since classical binary nucleation theory, with its well known inaccuracies, was used in the moment equations, the agreement between theory and experiment shown is thought to be satisfactory; agreement can be considerably improved by alterations of nucleation rates consistent in scale with reported deviations in experimental studies of homogeneous nucleation rates.

This dynamic aerosol model, BADM, is an option in AROSOL on the subgrid scale where dispersion and mixing of individual plumes can be accounted. The moments in the code are simply regarded as additional species subject to atmospheric transport with their kinetic equations as described above.

## SECTION 3

### RESULTS AND DISCUSSION

In a previous report<sup>3</sup>, we have presented an evaluation of AROSOL with the empirical model of Meaghers (EMM) for sulfate conversion using the EPA Philadelphia Aerosol Field Study Data (PAFS) data base. At that time, we did not investigate more detailed photochemical mechanisms, such as CBM or ALM, and we did not consider formation of nitrate aerosol. No information was available to us during this work on species such as ammonia and hydrocarbons in the emission inventory. Consequently, a detailed evaluation of AROSOL with the various available modules is not possible at this time. The purpose here is to test the performance of the chemical modules in AROSOL with the view of later evaluation should sufficient data become available.

In this section, we first discuss briefly the procedures followed in the earlier evaluation of AROSOL with EMM for sulfate conversion<sup>3</sup>. Next, we present a comparison of results for sulfate formation using EMM and CBM following the procedures outlined. This is followed by calculations using MARS for sulfate and nitrate speciation using available PAFS data. Finally, we present some comments on time and frequency response of chemical species in the CBM and ALM models.

### EVALUATION OF AROSOL USING PAFS DATA BASE

In previous work<sup>3</sup>, the AROSOL concentration predictions using the empirical model of Meaghers (EMM) were compared with PAFS measurements for four pollutant species: 1) Sulfur dioxide (SO<sub>2</sub>), 2) Lumped sulfate particles (fine + coarse), 3) Fine particle total mass, 4) Coarse particle total mass. Ten days out of the 31 days of the PAFS study were used for the evaluations, from 1st August to 10th August 1982. These days provided an unbroken record of measurements and contain no precipitation events. The fine and coarse sulfates were lumped together because the coarse sulfate emissions were assumed to be zero in the PAFS inventory.

The calculation grid was made up of 32x32 horizontal grids of size 2500m by 20 vertical layers of variable thickness depending on the mixing height. The southwest corner of the grid was set at UTM 444.5 E and UTM 4380.0 N, the domain covers 80x80 km which is just large enough to incorporate the entire PAFS emissions data set. The horizontal spacing corresponds to the size of the area source cells given in the PAFS

inventory and provides reasonable computation times. A diagram of the horizontal grids, the location of the measuring stations and the urban area can be found in our earlier report<sup>3</sup>.

As stated in Section 4, AROSOL is an Eulerian grid model which requires source injection algorithms in order to simulate the spreading of a pollutant into a cell before advection and dispersion can take place. This model is very sensitive to the parameters used in these algorithms. The three main algorithms used are for plume rises of point sources and injection of point and area sources; a fourth considers fumigation of pollutants into the grid system from aloft.

In AROSOL, plume rises are estimated using the Briggs plume rise formulae given in the Texas Episodic Model. The formulae depend on whether the atmosphere is stable or unstable and the ambient temperature. Calculations are made for both buoyancy and momentum driven cases and then the larger of the two is used as the plume rise. A detailed description of these formulae is given in our report<sup>3</sup>.

Once the plume rise has been calculated, the injection algorithm is used to distribute the emissions among the grid cells. First the time taken for the pollutant to diffuse through a vertical height of twice the plume rise + stack height ( $z_{pr}$ ) is calculated as  $t_v = 0.25z_{pr}^2/K_z$  and also the time taken to fill a horizontal cell  $t_h = dx*dy/(16ln(K_h))$ . The shorter of these two times is used to calculate the downwind location from the source at which the injection will occur. This is considered to be the location at which a source could make a significant contribution to a receptor near the ground. The pollutant from the point source is then distributed through a vertical height equal to twice the plume rise + stack height with a gaussian distribution with sigma equal to  $K_z*X/U$  where  $X$  is the downwind distance from the source and  $U$  is the wind speed.

A comparison of the distribution from a single point source predicted by the model to an analytical solution of the transport equation gives results accurate to about 5-6% on an axis downwind from the source when a horizontal spacing of 500m is used. Crosswind from the source the results are poorer; the procedure for plume spread described gives a much too broad distribution compared to the analytical solution.

The PAFS emissions inventory show that the point source emission rates are much larger than the area source rates. However, in our earlier study<sup>3</sup>, we found that only one major point source gives a significant contribution of SO<sub>2</sub> to the urban area on a typical PAFS day, the remainder being frequently downwind of the city and outside our

modeling domain. The ground level concentrations from the point sources are larger at night than during the day, for two main reasons: 1. The Briggs formulae give much lower plume rises in stable conditions than unstable causing the amount of material reaching the ground to be higher at night when the atmospheric boundary layer is stable; 2. The plume injection algorithm distributes the pollutant material up to twice the plume rise or the mixing height whichever is lower. Frequently at night the mixing height is the lower, again increasing the ground level concentrations.

For area sources, the pollutant is distributed with a uniform distribution through a vertical height depending upon the emission rate. The heights used were as follows: 1) If the SO<sub>2</sub> emission rate exceeds 2g/s then SO<sub>2</sub>, sulfate and fine particulates are distributed uniformly through a height of 110m. 2) If the SO<sub>2</sub> emission rate is less than 2g/s then SO<sub>2</sub>, sulfate and fine particulates are distributed uniformly through a height of 20m. 3) All coarse particulates are distributed uniformly through a height of 20m.

The SO<sub>2</sub> emissions which exceed 2g/s are assumed to be from industrial sources which have heights of up to 50m or so. The pollutant material is then considered to diffuse through a height of 110m while still within a grid cell. The value of 110m for the vertical spread was chosen so as to reduce the SO<sub>2</sub> night time bias to near zero, since the value of the height used has a strong effect on the results and is poorly known. Lower emission rates are assumed to correspond to residential areas where building heights are approximately 10m. Coarse particulate emissions come mainly from paved roads at very low heights.

It was found necessary during our earlier model investigation to incorporate fumigation into AROSOL<sup>3</sup>. Each time the mixing height changes, the vertical layers are redistributed. The first few are kept fixed in height and then the rest are distributed up to the mixing height keeping a constant ratio of one to another as the mixing height changes. The concentrations at the new nodes are obtained by linear interpolation from the old values. When the mixing height lowers, the old concentration values above it are thrown away since these concentrations will have blown away overnight before the mixing height rises again. When the mixing height rises the values at nodes above the old mixing height are set to a constant value. This value is an input to the model which may vary from hour to hour. This procedure has not been examined with regard to its accuracy for nonlinear species.

Background concentrations were needed for all pollutant species as the background plays a significant role in the Philadelphia region. Two kinds of background were used, upwind pollutants advected through the region and fumigation of pollutants from aloft. Since no measurements of these quantities were provided they had to be estimated from the measurements at the PAFS stations. For each pollutant the lowest 12 hour average in a 24 hour period measured at one of the rural stations 8, 12, 28, and 34, was used as the upwind background.

The fumigation background was estimated from comparison of model predictions and observations on a typical day - August 2nd. The best results were obtained for values 4 times the upwind background and 8 times the upwind background between the hours of 0700 and 1000 in the morning. For SO<sub>2</sub> the upwind background was generally zero but a value of 28 µg/m<sup>3</sup> was found to give reasonable results for fumigation. These estimates were then used for the entire evaluation period since in PAFS it was not possible to obtain estimates for each day due to budget constraints.

These methods are subjective and represent the largest source of uncertainty; background concentrations represent 50-80% of the measured values of the pollutants and during the morning hours it was found to be impossible to obtain meaningful results without accounting for fumigation.

#### STUDY OF SECONDARY SULFATE AND NITRATE USING PAFS DATA

The data base from PAFS did not permit a complete evaluation of AROSOL with the various modules introduced since our last report. These modules include CBM, ALM, MARS, and BADM (the binary aerosol dynamics model). In this section we demonstrate the use of the CBM and MARS modules in AROSOL. We begin with a limited comparison of sulfate conversion as given by both EMM and CBM using AROSOL with the PAFS data base. With the aid of MARS, sulfate speciation as a result of the conversion calculated by CBM is given for the same period. Finally, nitrate speciation calculated by MARS is obtained for the same study period. In these calculations, we only accounted for sulfate and nitrate conversions in the PAFS study area and have ignored contributions of these quantities from background and fumigation sources. As stated above, background and fumigation accounted for 50 - 80% of sulfate during the 1982 PAFS study.

As stated above, the PAFS emission inventory did not include information on hydrocarbons. Accordingly, hydrocarbons were assigned in the general category of non-methane hydrocarbons (NMOC) from PAFS PEDCO data<sup>36</sup> according to the EKMA

procedure. We followed the same procedure used by Dunker et al<sup>37</sup> and assigned in CBM the PAFS PEDCO NMOC as 25% OLE, 75% PAR, 2% FORM, 3% ALD2. Data for NH<sub>3</sub> were entirely absent from our data bases. We therefore assumed a constant value of 5  $\mu\text{g}/\text{m}^3$  which is a reasonable average of values reported<sup>38</sup> as representative for urban areas. Water vapor concentration was also obtained from the PEDCO data. The remaining reactants in CBM were contained in the PAFS emissions inventory<sup>3</sup>.

The simulations discussed below were carried out on the University of Texas CRAY XMP computer. Exclusive of CBM and MARS, AROSOL is now 95% vectorized. The ratio of simulated to CPU times for AROSOL with CBM and MARS on the CRAY is approximately 70. Model studies with the full version of AROSOL are therefore relatively expensive. For this reason, we have carried out simulations for only a single day of 1982 PAFS for a 12 hour period beginning at midnight.

Fig. 6 shows sulfate isopleths due to sulfate conversion at 0800 LST on 8.2.88 during PAFS by the EMM and CBM models. The two contours are very similar and differ principally in the magnitudes of the sulfate concentrations.

Fig. 7 shows the hourly average secondary sulfate concentrations averaged over the six monitoring stations in the PAFS study on 8.2.82 as calculated by EMM and CBM. No background or fumigation sulfate are included in this comparison. It is evident that the EMM gives sulfate concentrations approximately 10 times those given by CBM. Owing to the lack of detailed NMOC data in PAFS, it is not possible to assess the meaning of this large difference in predicted sulfate levels.

Fig. 8 shows the partitioning of sulfate between gas phase and aqueous phase at 1200 LST in the PAFS study area as given by MARS using the CBM sulfate predictions. As would be expected, the gas phase sulfate is very small; virtually all the sulfate resides in the aqueous aerosol.

At the assumed NH<sub>3</sub> levels, on 8.2.82 MARS predicts that all the nitrate resides in the gas phase with no aqueous or particulate nitrate. The relative humidity during this period was approximately 50%, a value too small to shift the equilibrium toward aqueous phase ammonium nitrate. This is indicated in Fig. 9 showing nitrate as HNO<sub>3</sub> averaged over the six PAFS monitoring stations as a function of LST. The increase in nitrate follows the expected diurnal pattern. No background or fumigation nitrate estimates are included in Fig. 9. All the HNO<sub>3</sub> shown is derived from the CBM photolytic reaction mechanism.

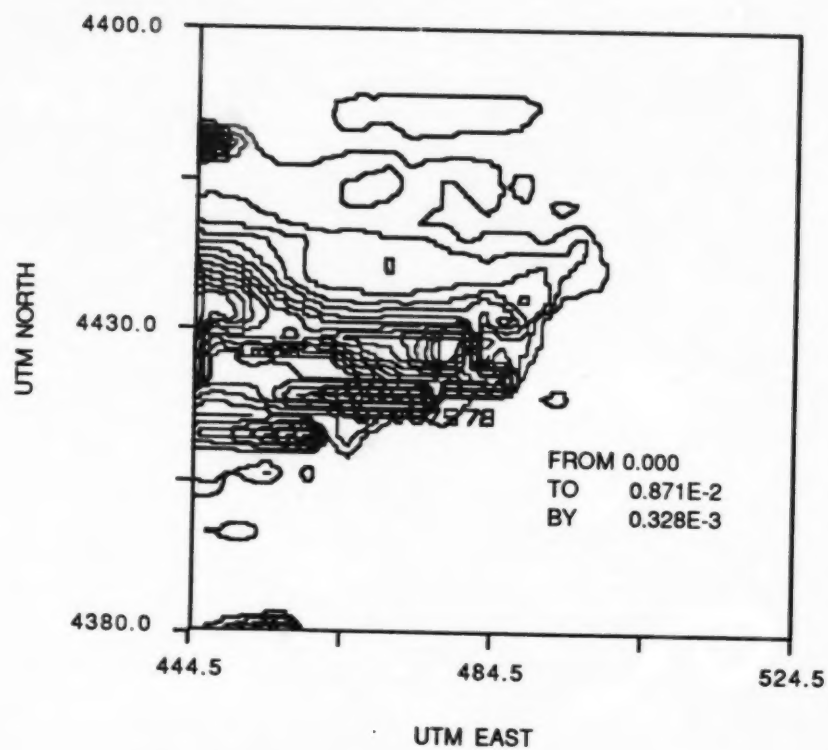


Fig. 6a. Sulfate concentration isopleths in PAFS study area on 8.2.82 at 0800 LST calculated by the EMM module in AROSOL

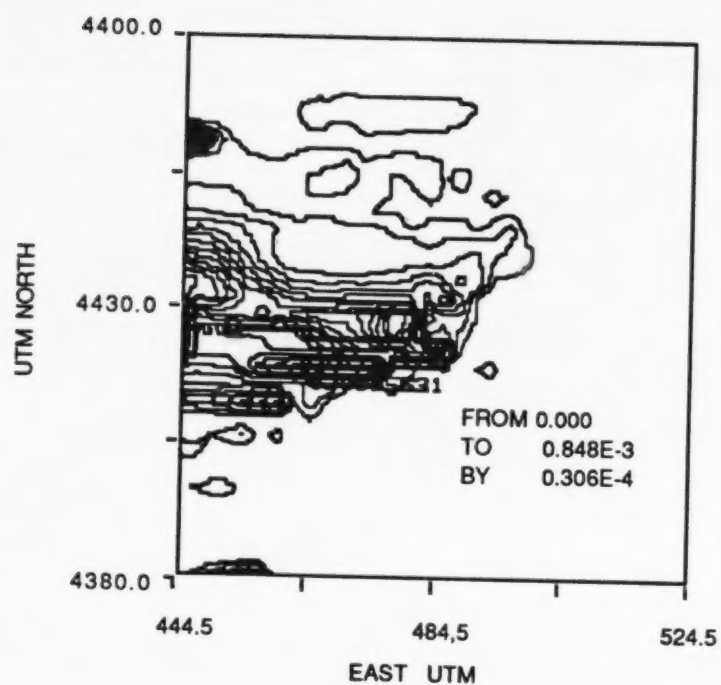


Fig. 6b. Sulfate concentration isopleths in PAFS study area on 8.2.82 at 0800 LST by the CBM module in AROSOL

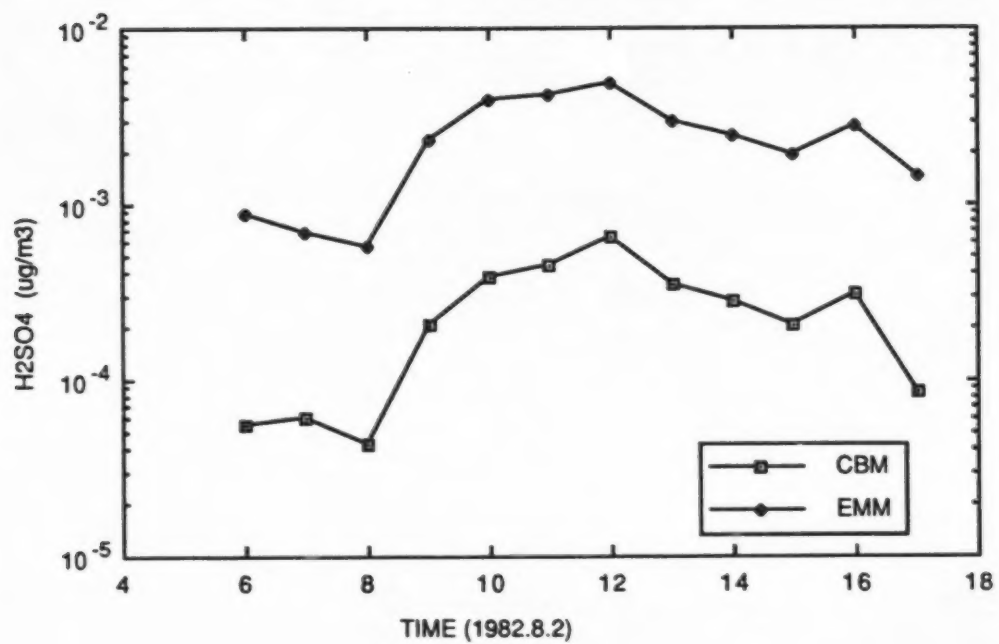


Fig. 7 Hourly average sulfate concentration as sulfuric acid averaged over the six PAFS stations as given by EMM and CBM. Times are LST.

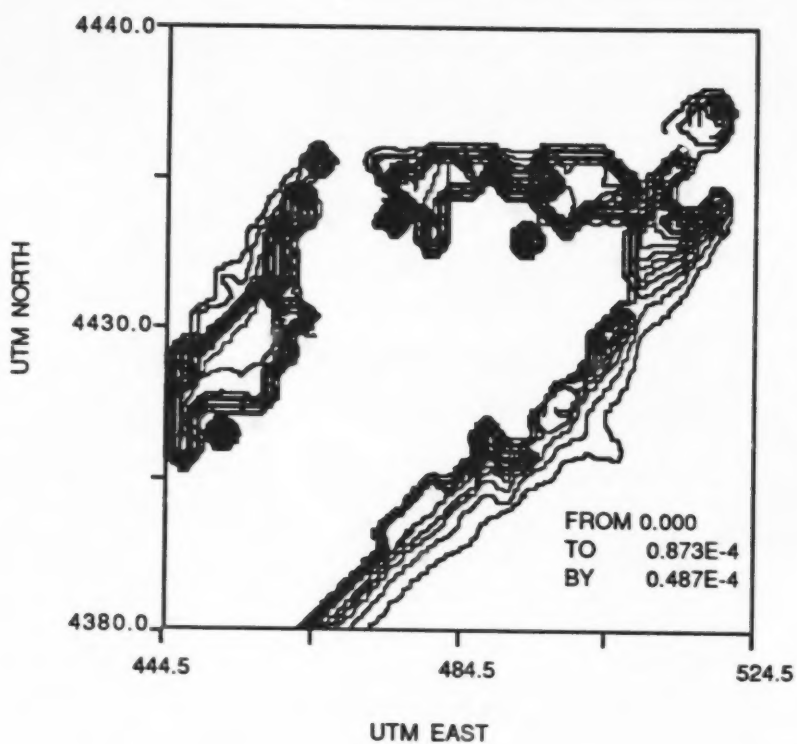


Fig. 8a. Hourly average secondary gas phase sulfate concentration isopleths in PAFS study area at 1200 LST as given by CBM and MARS. No background or fumigation sulfate has been included in this calculation.

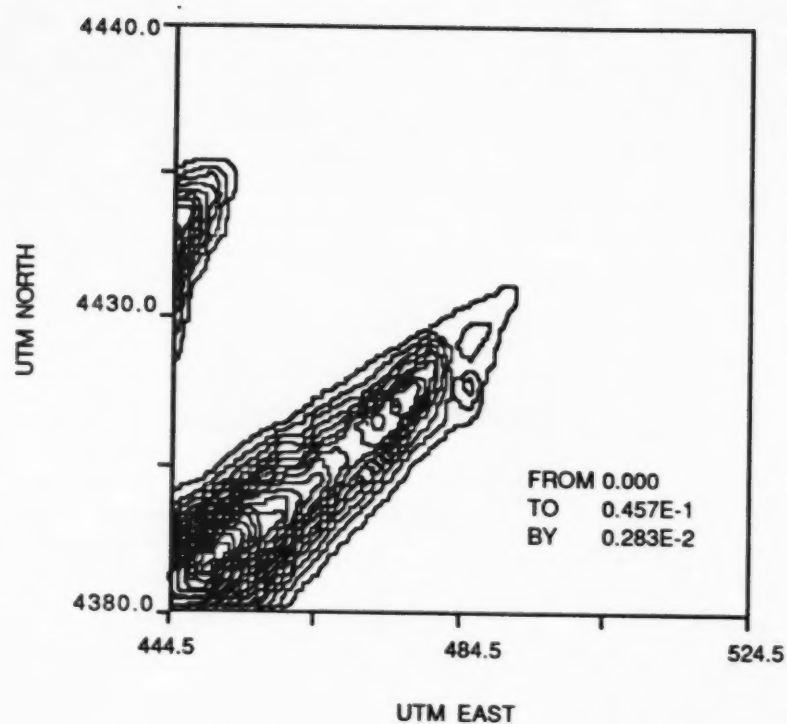


Fig. 8b. Hourly average secondary aqueous phase sulfate concentration isopleths in PAFS study area at 1200 LST as given by CBM and MARS. No background or fumigation sulfate has been included in this calculation.

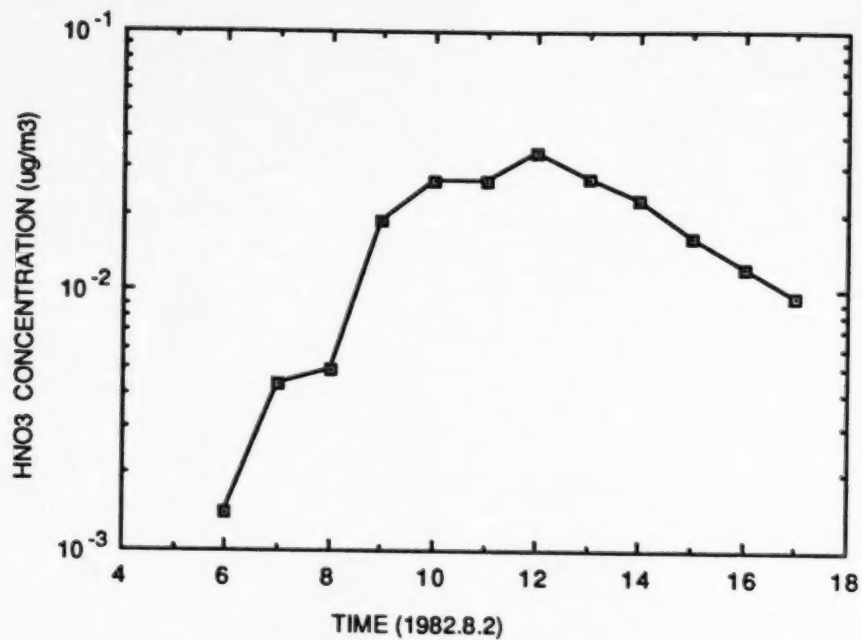


Fig. 9. Hourly average secondary gas phase nitrate concentrations as HNO<sub>3</sub> averaged over the six PAFS monitoring stations as a function of LST on 8.2.82 calculated according to CBM and MARS. No background or fumigation nitrate are included in this calculation.

## RESEARCH PROBLEMS IN URBAN AEROSOL MODELING

A great amount of time and money has been expended over the past several years for development of regional scale transport and transformation Eulerian models for application to such problems as acid deposition and nuclear winter. The development of RADM is a primary example of these relatively large scale efforts. Urban scale Eulerian models at present differ in large part only in scaling from the regional models. Urban scale aerosol models of the future most likely will need to deal more effectively with some essential problems characteristic of the urban scale. Two of these are: (1) Data bases resolved with small time and length scales; (2) Reaction and turbulent mixing at small time and length scales. The first of these will probably require advances in low cost field measurement technology. The second problem, in the context of Eulerian models, must involve development of subgrid scale models which account for the fact that in many urban areas pollutant transport and transformation involve reaction, mixing and entrainment by plumes. For example, many of the chemical reactions leading to secondary aerosol production have time scales less than or of the same order as the Lagrangian time scales of the turbulence so that the influence of turbulence on the reactions must be accounted.

We close this report with some remarks on a small subset of the second problem outlined above-- reaction and turbulent mixing at small time and length scales.

Both CBM and ALM are semiempirical models which attempt to overcome a number of problems in simulation of atmospheric photochemistry. For example, data bases do not resolve the many thousands of nonmethane organic compounds (NMOC) present in the atmosphere. Also, many thousands of rate equations would be needed to characterize the mechanisms of the photochemical reactions; their integration in the context of an Eulerian model would not be feasible with present computers. Such semiempirical models have been developed in part by introducing empirical parameters obtained with the aid of smog chamber data. Since the models contain empirical elements, their validity for urban simulations accounting for reaction and turbulent mixing does not appear to have been established.

We do not propose to solve this problem here. We merely emphasize the desirability of research which might lead to valid models for urban scale photochemical reactions applied in simulation of reaction in atmospheric turbulence. The current lumped parameter (semiempirical) models in use, such as CBM and ALM, have apparently not been tested for concentration fluctuations with frequencies characteristic of the urban scale. On this scale, reactive plumes in the atmosphere contain species subject to mixing and entrainment processes with time scales that may range from seconds to minutes and are subject to variations in solar flux with time scales also of seconds to minutes. In anticipation of the need, it would be useful to begin to direct some smog chamber and field studies toward obtaining the necessary information for semiempirical models suitable for reactive plume modeling.

## SECTION 4

### CONCLUSIONS AND RECOMMENDATIONS

The urban scale K theory model called AROSOL has been modified to include various modules for accounting for secondary aerosol formation, including the Empirical Model of Meaghers<sup>11</sup> (EMM), the Carbon Bond Mechanism<sup>14</sup> (CBM-IV), the Atkinson Lloyd Mechanism<sup>13</sup> (ALM, 1985 ERT version), the Model for an Aerosol Reacting System<sup>4</sup> (MARS), and the Binary Aerosol Dynamics Model<sup>33</sup> (BADM). In a previous report<sup>3</sup>, we have presented an evaluation of AROSOL with the empirical model of Meaghers (EMM) for sulfate conversion using the EPA Philadelphia Aerosol Field Study Data (PAFS) data base. At that time, we did not investigate more detailed photochemical mechanisms, such as CBM or ALM, and we did not consider formation of nitrate aerosol. The PAFS data base does not have information on species such as ammonia and hydrocarbons in the emission inventory and no measurements of ammonia, hydrocarbon speciation, and nitrates were made. Consequently, a detailed evaluation of AROSOL with the various available modules has not been possible at this time. Here we have tested the performance of the chemical modules in AROSOL with the view of later evaluation should sufficient data become available.

In comparison of sulfate formation based on the PAFS data base, we have found that EMM gives sulfate concentrations approximately 10 times those given by CBM. Owing to lack of hydrocarbon speciation in the PAFS data base, it is not possible to assess the meaning of the large difference. However, EMM is entirely empirical and cannot be expected to apply reliably to a specific location and time period. For the same data sets, the ALM was found to give consistently higher values of sulfate and nitrate than did CBM, a result consistent with previous findings. The module MARS for estimating equilibrium phase relationships between sulfates, nitrates, ammonium and ammonia was implemented and found to be efficient, requiring only about 5% of the CPU time. However, MARS has evidently not been subjected to suitable evaluation in urban scale simulations; in particular, the role of other species such as oxygenated organic compounds and various additional cations and anions on the equilibrium phase relationships may need to be examined. On the University of Texas CRAY XMP computer, urban scale simulations based on the PAFS data base using AROSOL with CBM and MARS required ratios of simulated to CPU times in the range 50 - 70.

A major difficulty in this model study was the large sulfate and nitrate background during the PAFS period. For model input it was necessary to estimate

background concentrations from a limited number of PAFS stations outside the modeling domain. For fumigation, no measurements were available and estimates had to be made from comparison of model predictions and observations for a "typical" day. In the future, field studies should be designed to obtain reasonable estimates of background and fumigation for all model input species.

In all the simulations with CBM for sulfate, low sulfate formation in the modeling domain was found. A number of possible reasons may be cited. First, inaccuracies are now known to be present in the hydrocarbon data from PAFS; water interferences occurred in the analyzers, resulting in model input hydrocarbon values that are too low. Therefore, the resultant simulated sulfate conversion/deposition rates are too small. Also, with limited data on hydrocarbon speciation available, assumptions according to the EKMA procedure were necessary; these assumptions may not have been valid for the modeling domain. Finally, the large differences in sulfate conversion given by the CBM and ALM models suggest uncertainties in these photochemical models.

For advance in urban aerosol modeling a number of research problems have been noted. These include development of field measurement technology to permit acquisition of urban data bases with small time and length scales. For example, reliance on usually inadequate emissions inventories and point source measurements introduces major uncertainties in modeling studies. A second problem pertinent to urban scale modeling is the development of subgrid models to account for reaction and turbulent mixing at small time and length scales. In this regard, the current lumped parameter (semiempirical) chemistry models, such as CBM and ALM, have apparently not been tested for concentration fluctuations with frequencies characteristic of the urban scale. On this scale, reactive plumes in the atmosphere contain species subject to mixing and entrainment processes with time scales that may range from seconds to minutes and are subject to variations in solar flux with time scales also of seconds to minutes. Failure to account for these fluctuations can result in large errors in calculated formation rates of species such as sulfates and nitrates.

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